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Effect of curing temperature, fibre loading and bonding agent on the equilibrium swelling of isora-natural rubber composites

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Abstract—Isora fibre-reinforced natural rubber (NR) composites were cured at 80, 100, 120 and 150°C using a low temperature curing accelerator system. Composites were also prepared using a conventional accelerator system and cured at 150°C. The swelling behavior of these composites at varying fibre loadings was studied in toluene and hexane. Results show that the uptake of solvent and volume fraction of rubber due to swelling was lower for the low temperature cured vulcanizates which is an indication of the better fibre/rubber adhesion. The uptake of aromatic solvent was higher than that of aliphatic solvent, for all the composites. As the fibre content increased, the solvent uptake decreased, due to the superior solvent resistance of the fibre and good fibre–rubber interactions. The bonding agent improved the swelling resistance of the composites due to the strong interfacial adhesion. Due to the improved adhesion between the fibre and rubber, the ratio of the change in volume fraction of rubber due to swelling to the volume fraction of rubber in the dry sample (V_r) was found to decrease in the presence of bonding agent. At a fixed fibre loading, the alkali treated fibre composite showed a lower percentage swelling than untreated one for both systems showing superior rubber–fibre interactions.

Keywords: Composites; equilibrium swelling; interfacial adhesion; isora fibre; bonding agent; reinforcement.

1. INTRODUCTION

There have been several attempts to utilize the abundant and renewable resources of plant fibres to develop environmentally advantageous composite materials [1]. With their low cost and high specific mechanical properties, they represent a good, renewable and biodegradable alternative to the most common synthetic

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*To whom correspondence should be addressed. E-mail: rani@cusat.ac.in reinforcement. The reinforcement of polymer matrices with natural fibres was considered to be difficult due to the lack of adhesion with polymeric matrices. Experimental studies have shown that control of fibre–matrix interfacial bond strength is a critical factor in obtaining the best mechanical properties out of the resultant composite material [2]. Typically, physical and chemical [3–8] modifications of fibres and matrices have been performed in order to obtain better surface properties of the composite constituents. Rubber–fibre composites are used in the rubber industry because of the advantages they impart in processing and low cost coupled with high strengths. Normally, a rubber–fibre composite can offer a set of properties that may give it the potential of entering application areas not possible with either of the components in the composite [9]. These composites combine the elastic behavior of rubber with the strength and stiffness of fibre. Several researchers have studied the properties of various cellulosic fibre elastomer composites [10–16] and found that the aspect ratio of the fibre and its chemical treatment has a major influence on composite properties. The natural fibre under consideration here is isora fibre, a bast fibre separated from the bark of the *Helicteres isora* plant by a retting process. Isora shrubs grow in many parts of South India, especially in Kerala. Isora resembles jute in appearance, but surpasses it in strength, durability and lustre. The properties of isora are comparable to those of other natural fibres like sisal, jute, etc. Recently, high performance cost effective composites have been developed by the incorporation of isora fibres into NR matrix in this laboratory [17, 18]. The effect of chemical treatment on the mechanical behavior [17] and the effect of high-energy radiation, ozone and heat on the degradation behavior [18] of these composites were also reported. Effects of low temperature curing on the mechanical performance of these composites have also been investigated [19]. It has been observed that the low temperature curing is more effective for the composite in getting desirable mechanical properties. It is likely that at high temperature the fibre shows a tendency to undergo degradation. In order to analyze the service performance of rubber composites when in contact with solvents, the solvent resistance of such composite is also important [20–22]. An important difference between vulcanized and raw rubber is that the former possesses a structure, which cannot be broken down completely by any solvent. The material therefore swells and cannot be dispersed. The contact of rubbers with organic solvents can be well explained by absorption and diffusion phenomena [23]. Numerous techniques like H-block and strip adhesion, both dynamic and static in nature, have been used to measure adhesion between fibre and rubber. While most of these techniques give a good relative indication of adhesion, the time-dependent nature of the viscoelastic materials overshadows the real effect. Equilibrium swelling is another technique, which has been used to assess the fibre–rubber adhesion. Fibres, if bonded effectively, are supposed to restrict the swelling of elastomers. The adhesion between rubber and various synthetic fibres like glass, asbestos, and natural fibres like sisal, oil palm, etc. have been studied using restricted swelling measurements [13, 24–26]. In this paper we describe a study of the swelling behavior of short isora fibre-reinforced natural rubber composites. The effects of fibre loading, chemical modification of the fibre and presence of bonding agent on the swelling behavior of isora-NR composites vulcanized at low and high temperatures are proposed to be investigated.

2. EXPERIMENTAL

2.1. *Materials*

The raw isora fibre used in the study was separated from the bark of the *Helicteres isora* plant by a retting process. Then it was chopped to an average length between 9 to 11 mm and designated as untreated fibre. The properties of isora fibre in comparison with other natural fibres are given in Table 1, which clearly indicates that isora fibre has properties comparable to other natural fibres like sisal, jute, etc. The NR used was supplied by RRII (Rubber Research Institute, India) Kottayam. The solvents are of reagent grade and were distilled before use. The bonding agent (RF resin : Hexa : Silica) and all other ingredients used were commercial grade.

2.2. *Chemical treatment of the fibre*

This was carried out by mercerization. Untreated short fibres of an average length of 10 mm were immersed in 5% aqueous NaOH for 3 to 4 h, then washed with water and dried in an air oven at 70°C.

2.3. *Composite preparation*

Short isora fibres, both alkali-treated and untreated, have been incorporated into NR at different fibre loadings on a laboratory two-roll mill and vulcanized using conventional and low temperature curing accelerator systems based on the formulation given in Table 2. Details of mixing and processing of these composites have been reported elsewhere [17, 18].

Table 1.
Comparison of the properties of isora and other natural fibres

Fibre	Diameter (μm)	Micro fibrillar angle (deg)	Cellulose/lignin content (%)	Tensile strength (MPa)	Density (g/cm^3)
Isora	10–20	20–25	75/23	500–600	1.35
Coir	100–460	30–49	43/45	130–170	1.15
Sisal	50–200	10–22	67/12	400–600	1.45
Oil palm	50–500	40–46	65/19	200–250	1.45
Jute	12–25	8–10	63/12	430–530	1.45
Banana	80–250	10–15	65/5	500–700	1.35

Table 2.
Compound formulation (phr)

Ingredients	X10	X20	X30	X40	X10b	X20b	X30b	X40b	Y30	Y30b
RF resin	—	—	—	—	2.5	5.0	7.5	10	—	7.5
Silica	—	—	—	—	1.0	2.0	3.0	4.0	—	3.0
Hexa	—	—	—	—	1.6	3.2	4.8	6.4		4.8
Fibre [U]	10	20	30	40	10	20	30	40	30	
Fibre [T]	—	—	—	—	—	—	—	—	—	30

Basic recipe: NR-100, ZnO-5.0, stearic acid-2.0, TDQ-1.0, S-2.5 low temp curing system (ZDC-1.0, xanthate-0.75) for the conventional system (CBS-0.6, TMTD-0.1). Conventionally cured composites are represented by X_0 e.g.; $X_0$30b-30 phr loading with bonding agent cured by conventional systems.

2.4. Sorption experiments

Circular specimens of diameter 20 mm were punched out from the vulcanized sheets. Thicknesses and diameters of the specimens were measured by means of a screw gauge and vernier calipers, respectively. Specimens of known weight were immersed in the solvents (toluene and hexane) in diffusion test bottles and kept at room temperature. Samples were removed from the bottles at periodic intervals and the wet surfaces were quickly dried using tissue paper and the weights of the specimen after swelling were determined at regular intervals until no further increase in solvent uptake was detected. Thickness and diameter of the specimen after equilibrium swelling were also measured.

2.5. Swelling data analysis

The swelling parameters like mol% uptake of solvent, and change in the volume fraction of rubber due to swelling were calculated.

2.5.1. Calculation of Q_t (mol% uptake of the solvent). The mol% uptake of the solvent Q_t for the composite samples was determined using the equation

$$Q_t = \frac{(W_2 - W_1/M_s)}{W_1} \times 100, \tag{1}$$

where W_1 and W_2 are the weights of the specimen before and after swelling, and M_s is the molar mass of the solvent. The sorption data were evaluated by plotting the mol% uptake (Q_t) of the solvent *versus* the square root of time for different solvents.

2.5.2. Calculation of V_τ (Ratio of the change in the volume fraction of rubber due to swelling). To determine the volume fraction of rubber in the unswollen vulcanizates, the test specimens were weighed both in air and in water. Using the base formulation the amount of rubber present in the weighed samples and its volume were calculated. From these data the volume fraction of rubber present in the unswollen sample V_i was calculated. The volume fraction of rubber in the swollen sample V_f was calculated by the expression

$$V_f = \frac{[(D - FT)/(d_r)]}{[(D - FT)/(d_r)] + [A_o/d_s]}, \qquad (2)$$

where d_r and d_s are the densities of the rubber and solvent, D is the deswollen weight of the test specimen (dry weight), F is the weight fraction of the insoluble components, T is the weight of the specimen and A_o is the weight of the absorbed solvent corrected for swelling increment respectively.

The ratio of the change in the volume fraction of the rubber due to swelling was calculated as

$$V_{\tau} = (V_i - V_f)/V_i, \qquad (3)$$

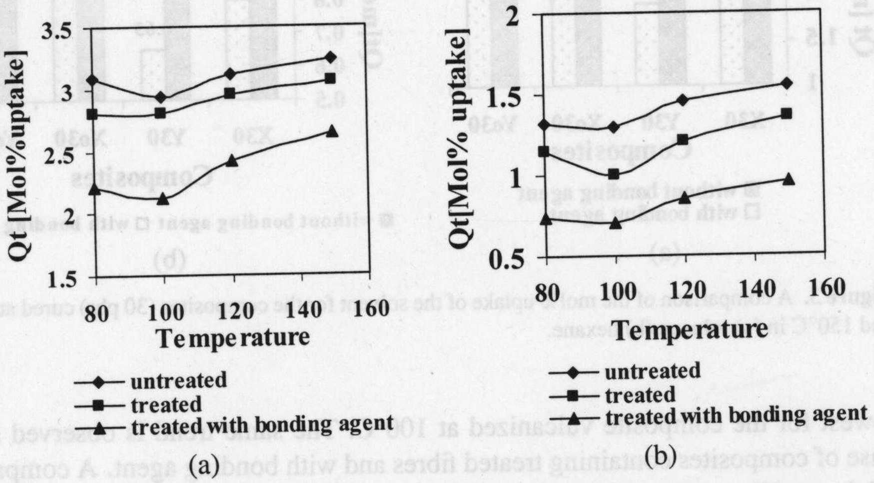
where V_i is the volume fraction of rubber in the unswollen sample, V_f is the volume fraction of rubber in the swollen sample.

2.5.3. Optical and SEM studies. The physical nature of the composite samples before and after sorption studies was analyzed using an optical microscope. Treated and untreated fibre surfaces were examined by a JEOL JSM 35 C model scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

3.1. Effect of curing temperature

Figures 1 and 2 show the variation of the mol% uptake in toluene and hexane with curing temperature of the composites. In both solvents the uptake of solvent is



(a) (b)

Figure 1. Variation of mol% uptake of solvent with curing temperature of the composites in (a) toluene (b) hexane.

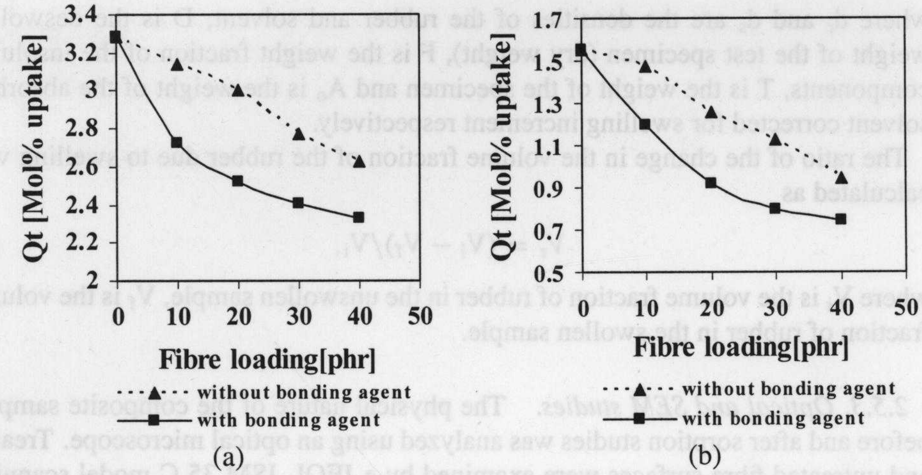


Figure 2. Effect of fibre loading on equilibrium sorption of NR/isora composites with and without bonding agent cured at 100°C in (a) toluene (b) hexane.

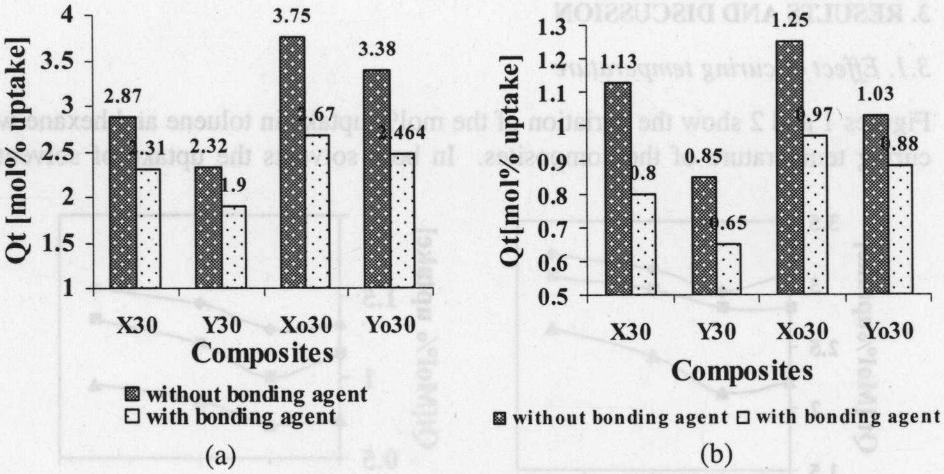


Figure 3. A comparison of the mol% uptake of the solvent for the composites (30 phr) cured at 100°C and 150°C in (a) toluene (b) hexane.

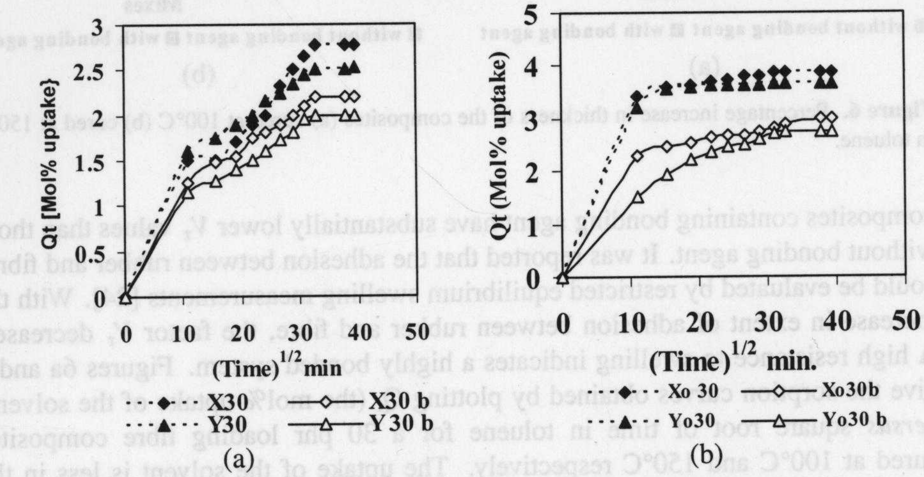
lowest for the composite vulcanized at 100°C. The same trend is observed in the case of composites containing treated fibres and with bonding agent. A comparison of the mol% uptake of the solvent for the composites cured at 100°C and 150°C is given in Fig. 3. It may be observed that the uptake of solvent is high for the composites cured at high temperature (150°C). This shows that the reinforcement is most effective when the composite is cured at 100°C and it is likely that at higher temperature (150°C) the fibre and rubber shows a tendency to degrade as evident from the results of our previous studies [19].

3.2. Effect of fibre loading and bonding agent

Figures 4 and 5 give the variation of mol% uptake of the solvents (toluene and n-hexane) with fibre loading for both systems. For the composites cured at both temperatures it is clear that, as fibre loading increases, equilibrium solvent intake decreases. This is obviously due to the increased hindrance exerted by the fibres at higher loadings. From Figs 4 and 5 it is clear that for the composites containing bonding agent there is a sharp decrease in the uptake of solvents. A highly bonded system would exhibit high resistance to swelling compared to the unbonded systems.

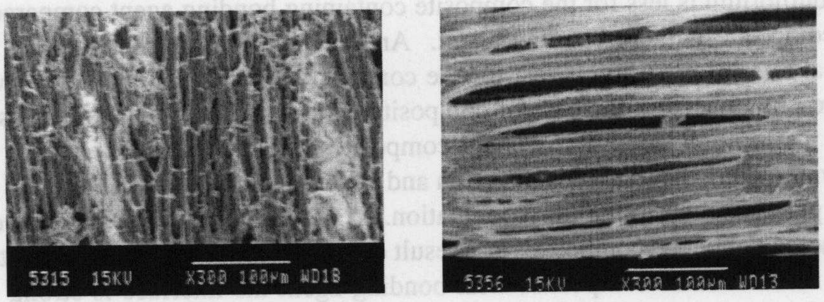
3.3. Correlation with adhesion

Table 3 gives the change in volume fraction of the rubber due to swelling (V_τ) for mixes containing different loading of fibres for both systems. It is evident that the



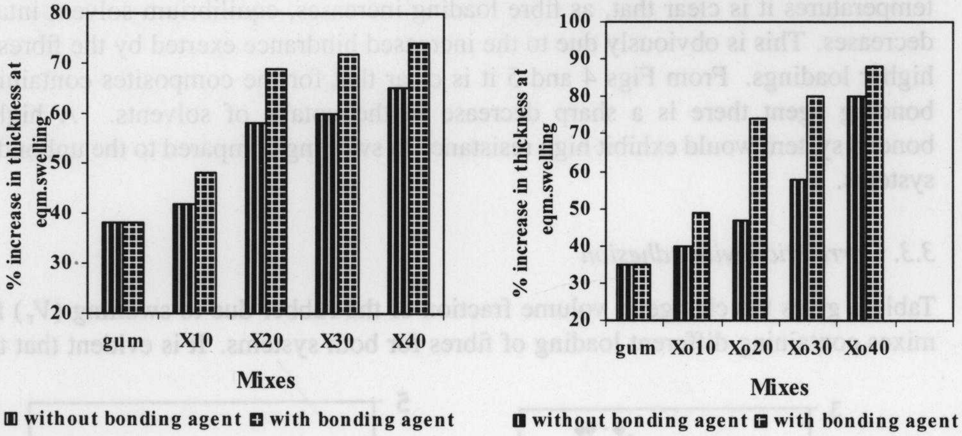
(a) (b)

Figure 4. The equilibrium sorption curves of the mixes (a) cured at 100°C (b) cured at 150°C in toluene at 25°C.



(a) (b)

Figure 5. SEM photographs of (a) untreated isora fibre (b) alkali-treated isora fibre at a magnification of ×300.



(a) (b)

Figure 6. Percentage increase in thickness of the composites (a) cured at 100°C (b) cured at 150°C in toluene.

composites containing bonding agent have substantially lower V_τ values than those without bonding agent. It was reported that the adhesion between rubber and fibres could be evaluated by restricted equilibrium swelling measurements [24]. With the increase in extent of adhesion between rubber and fibre, the factor V_τ decreases. A high resistance to swelling indicates a highly bonded system. Figures 6a and b give the sorption curves obtained by plotting Q_t (the mol% uptake of the solvent) *versus* square root of time in toluene for a 30 phr loading fibre composites cured at 100°C and 150°C respectively. The uptake of the solvent is less in the case of composite cured at 100°C, which shows the better reinforcement at low temperature. At the same fibre loading, the amount of solvent sorbed by a composite at equilibrium is less for the composite containing bonding agent compared to that of composite without bonding agent. Another interesting observation is that the initial rates of diffusion is fast for the composite without bonding agent, which is more pronounced in the case of composite cured at 150°C. This is because of the fact that, in unbonded fibre–rubber composites, the solvent can penetrate into the polymer along the thickness direction and also through the weak interfaces parallel and perpendicular to the fibre orientation. The initial driving force for swelling is higher in unbonded composites as a result of large number of voids at the interfaces. But in the case of composites with bonding agent the interface is strong and the liquid can penetrate into the polymer only through the space between the fibre ends. As a result, the diffusion rate is slow in well bonded composites. The same observations have also been reported in the case of sisal rubber composites [26]. The uptake of aliphatic solvent is less than that of aromatic solvent. Normal hexane, which is puckered in nature, presents greater surface area than toluene, which is planar. Hence it is more difficult for hexane to penetrate into the composite than toluene with the result that the solvent uptake is less for hexane.

Table 3.
Change in the volume fraction of rubber due to swelling for the composites cured at 100°C and 150°C

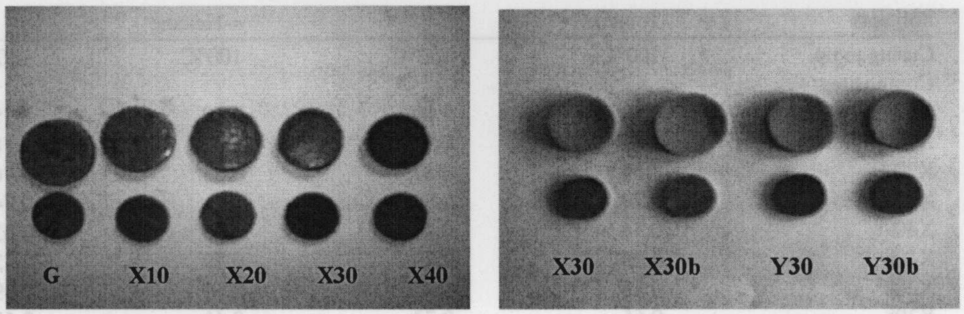
	Ratio of the change in volume fraction of rubber due to swelling (V_τ)			
Solvents	Toluene		n-Hexane	
Curing temp.	100°C	150°C	100°C	150°C
Composites				
GUM	0.94	1.09	0.70	0.79
X10	0.89	0.93	0.65	0.78
X20	0.83	0.87	0.63	0.76
X30	0.79	0.83	0.61	0.74
X40	0.76	0.80	0.55	0.63
X10b	0.85	0.89	0.59	0.73
X20b	0.73	0.85	0.50	0.69
X30b	0.65	0.73	0.41	0.60
X40b	0.55	0.70	0.38	0.48
Y30	0.69	0.76	0.59	0.64
Y30b	0.55	0.65	0.40	0.50

3.4. Effect of chemical treatment

The effect of chemical treatment of fibres on equilibrium swelling of the composites can also be seen from the Figs 3 and 4. It is observed that in composites containing treated fibres, the solvent uptake is reduced further, which is due to the enhanced interfacial bonding between the fibre and rubber. This prevents the transport of solvent to some extent through the interface. The surface topology of the untreated fibre is shown in Fig. 5a. The fibrillar nature as well as the porosity of the fibre is revealed from the fibre topography. The porous surface morphology is useful to have better mechanical interlocking in the matrix for composite fabrication. The fibre shows an uneven surface due to protrusions constituted of hemicellulose and pectin. The surface contains a waxy cuticle layer also, which also prevents a better interlocking with the rubber. On alkali treatment, due to the dissolution of impurities and waxy materials from the surface, the pores become more significant and fibres become thinner than the untreated fibre (see Fig. 5b). This renders roughness to the fibre thereby enhancing the mechanical interlocking at the interface. Thus it is clear that equilibrium liquid uptake can provide information regarding the efficiency of interfacial bonding. On comparing the equilibrium uptake of composites containing treated and untreated isora fibres it can seen that the former composites are better than the latter in resisting the uptake of both solvents, as evident from the Figs 3 and 4 of both systems.

3.5. Dimensional changes of the composites

The percentage increase in thickness at equilibrium swelling in toluene is shown in Figs 6a and 6b for the composites cured at 100°C and 150°C, respectively. It is observed that the change in thickness is higher for the composite containing the



(a) (b)

Figure 7. Optical photographs of the samples (a) cured at 100°C (b) cured at 150°C before and after swelling in hexane at 25°C (mixes defined in Table 2).

bonding agent and it increases with fibre loadings. In a well-bonded, oriented fibre rubber composite, the swelling is anisotropic. It will swell to a greater extent in a direction perpendicular to the fibre orientation. This is because the oriented fibres will prevent the penetration of the liquid in the direction perpendicular to the flat surfaces of the specimen. Hence, the solvent can diffuse into the polymer only through a direction parallel to fibre orientation. Thus, swelling was considered to be constrained in one direction and as a result the thickness of the specimen increased considerably and the diameter change was negligible as circular specimens were used. The percentage increase in thickness was found to be higher for the composite cured at higher temperature (150°C) as evident from the figure. This also accounts into the better reinforcement of the composite cured at lower temperature.

The optical photographs of the unswollen and swollen samples of varying fibre loadings cured at 100°C in hexane are shown in Fig. 7a. From the figure it is clear that as fibre loading increases, the diameter of the swollen samples decreases. At the same fibre loading (30 phr), the diameter of the bonded composite is lower than that of the unbonded composite, as evident from Fig. 7b. From this it is evident that in highly bonded composites swelling occurs predominantly in the thickness direction. Thus the restricted equilibrium swelling can be used to measure the extent of interfacial bonding between the fibre and rubber.

4. CONCLUSIONS

The equilibrium swelling behavior of short isora fibre-reinforced natural rubber composites was investigated with special reference to the curing system, curing temperature, effects of fibre loading, chemical treatment of fibres and bonding agent. The following conclusions can be drawn from this study.

Composite cured at 100°C shows lower equilibrium swelling in solvents like toluene and hexane compared to that cured at 150°C.

The uptake of aromatic solvent is higher than aliphatic solvent. For the rubber compound containing a bonding agent, the equilibrium swelling is substantially lower than that of the composite without a bonding agent. It is again lower for the composite containing bonding agent cured at lower temperature.

Increased fibre loading brings about greater restriction to swelling for both types of composites cured at normal and lower temperature.

Swelling data values and dimensional changes (thickness and diameter) provide valuable information on the interface adhesion.

Alkali-treated fibre composites with bonding agent absorb less solvent compared to composites containing untreated fibre without bonding agent indicating that alkali treatment and presence of bonding agent improve adhesion between rubber and fibre.

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